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LIMITATIONS IN DTA INVESTIGATIONS OF THE SYSTEM $RbCl/LaCl_3$

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SUMMARY

The hydrated lanthanous double chlorides $CsLaCl_4 \cdot 3H_2O$ and $RbLaCl_4 \cdot 4H_2O$ can be partially dehydrated to compounds $ALaCl_4 \cdot 0.5H_2O$. The complete degradations yield a mixture of $Cs_2LaCl_5 + CsLa_2Cl_7$ in the case of the Cs-compound, while ($Rb_2LaCl_5 + LaCl_3$) is formed from the Rb-compound. By DTA the formation temperature of $RbLa_2Cl_7$ - metastable at ambient temperature - was found at 371° C.

INTRODUCTION

In an article in J.Therm.Anal. (ref.1) we have previously comprehended retarded solid state reactions occuring in the systems of alkalimetal chlorides with trichlorides of the early lanthanoides. We could demonstrate that reconstructive phase transitions or solid state formation and decomposition reactions may be so much retarded that they don't occur at all in cooling experiments. Therefore, they cannot be detected by DTA- and X-ray- measurements. A good example is the compound $KMnCl_3$ (ref.2). It is crystallizing from the melt with the cubic perovskite-structure and is then undergoing several non-reconstructive phase transitions to distorted perovskites. At ambient temperature the $GdFeO_3$ - structure exists, however, only metastable. As investigations in Israel had shown (ref.3), a transition to the stable modification with the NH_4CdCl_3- structure had occured in three years to such an amount, that it could be detected by X-ray reflection. A way to yield this phase quantitatively is the dehydration of $KMnCl_3 \cdot 2H_2O$ at 120°C. We found by DSC that the transition to the high-temperature modification occurs at 267°C with an enthalpy of 4.60 $kJ \cdot mole^{-1}$ (ref.2).

A somewhat other problem arose in the system $RbCl/LaCl_3$ (ref.4): According to EMF vs.T-measurements, carried out in a galvanic formation cell with solid electrolytes, we determined the function $\Delta G=f(T)$ and found, that the compound $RbLn_2Cl_7$, which is stable at high temperature, should decompose at 353° C.

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For the synproportionation 0.25 Rb_2LaCl_5+0.75 $LaCl_3$=$Rb_{0.5}LaCl_{3.5}$ we had found $\Delta G/ KJ\cdot mole^{-1}=6.2 -0.0099\cdot T/K$ with $\Delta G=0$ at 626K (353°C).

With DTA, no thermal effect could be detected, neither after annealing for one month at ~320°C. A hydrate of this substance is not known, however, a compound $RbLaCl_4\cdot 5H_2O$ is described in literature (ref.5). It was now of special interest which phases would be formed by dehydration, because an anhydrous $RbLaCl_4$ is not known. Either Rb_2LaCl_5 together with metastable $RbLa_2Cl_7$ or with $LaCl_3$ might be formed. In both cases DTA heating experiments should give an effect for the reaction at 353°C. We have completed these investigations, by considering the systems with CsCl too, where we had found a compound $CsLa_2Cl_7$, stable at ambient temperature.

EXPERIMENTAL

For the preparation of the hydrates La_2O_3 (99,99%, Fa C. Roth, Karlsruhe) was dissolved in hydrochloric acid. RbCl and CsCl were of p.a.-quality (Fa. Merck, Darmstadt).

Thermogravimetic decomposition curves were measured with the thermobalance TG-750 of Stanton Redcroft, DTA-heating curves with a home-built device, described elsewhere (ref.7). X-ray powder patterns were taken with a Philips pW 1050/25 goniometer, equipped with a proportional counter (Cu-K_α radiation, samples under He atmosphere). - Single crystal measurements: Two cycles' goniometer STADI 2 and Lattice explorer (Fa. Stoe, Darmstadt).

THE HYDRATES

According to literature hydrates $ALaCl_4\cdot xH_2O$ (A=Cs[5], Rb[6]) exist as congruently soluble compounds. We isolated the hydrates $CsLaCl_4\cdot 3H_2O$ and $RbLaCl_4\cdot 4H_2O$ by slowly evaporating aqueous solutions with ACl and $LaCl_3$-contents in the molar relation 1:1 at ~35°C. The needlelike crystals were dried by washing with ether.

From single-crystal X-ray photos the unit cells of both compounds could be determined.

$CsLaCl_4\cdot 3H_2O$: monoclinic, a=7.135 (2) Å; b=8.694 (4) Å; c=8.080 (2) Å; ß=99.36 (2)°; Z=2.
d_x=3.14 $g\cdot cm^{-3}$; internal standard: CsCl with a=4.123 Å (d-spacings of the first 20 hkl in table 1).

$RbLaCl_4\cdot 4H_2O$: orthorhombic, a=11.414 (5) Å; b=6.698 (2) Å; c=7.028 (3) Å; Z=2.
d_x=2.71 $g\cdot cm^{-3}$; internal standard: Al_2O_3 with a=4.75917 Å; c=12.98997 Å.

The complete structure determination of the Rb-compound (space group $P2_12_12$) will be described elsewhere.

As found by non-isothermic measurements in a thermo-balance (fig.1), the dehydration of both substances occurs in several steps. The intermediate hydrates were prepared as follows:

TABLE I

Powder data for $CsLaCl_4 \cdot 3H_2O$ (monoclinic cell)

h k l	d/Å	100 I/I (111)	h k l	d/Å	100 I/I (111)
001	7.980	65	012	3.626	40
100	7.040	30	200	3.520	25
10-1	5.765	70	12-1	3.471	15
110	5.471	45	11-2	3.435	90
101	4.900	20	20-1		
11-1	4.805	85	210	3.257	40
020	4.347	25	012		
111	4.268	100	21-1	3.193	50
020	3.990	20	112	3.044	70
10-2	3.742	20	201		

$RbLaCl_4 \cdot 4H_2O \longrightarrow RbLaCl_4 \cdot 3H_2O$: 7g in an Ar-stream at 105°C for 1h.
$ALaCl_4 \cdot 3H_2O \longrightarrow ALaCl_4 \cdot 0.5H_2O$ (A=Cs,Rb): 2h, Ar-stream at 150°C.
Total dehydration: 2h in an HCl-stream at 250 C.

It should be pointed out that the structure of $RbLaCl_3 \cdot 3H_2O$ seems not to be isotypic with those of the analogous Cs-compound. - Powder diffractograms of the semihydrates are displayed in fig.2.

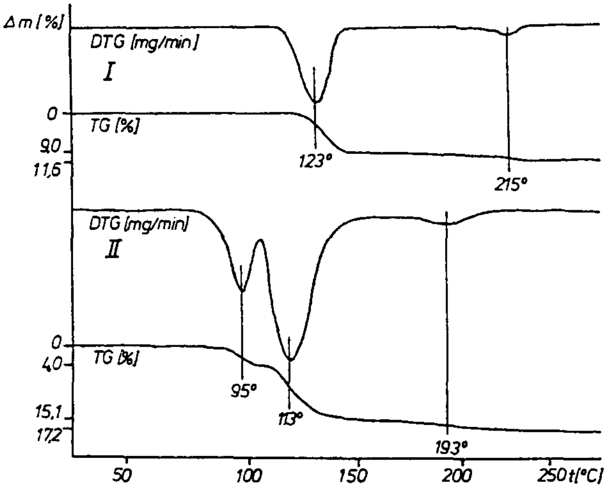

Fig.1. TG and DTG curves for the degradation of $CsLaCl_4 \cdot 3H_2O$ (I) and $RbLaCl_4 \cdot 4H_2O$ (II) (Heating rate=5 deg.min^{-1}; Ar atmosphere)

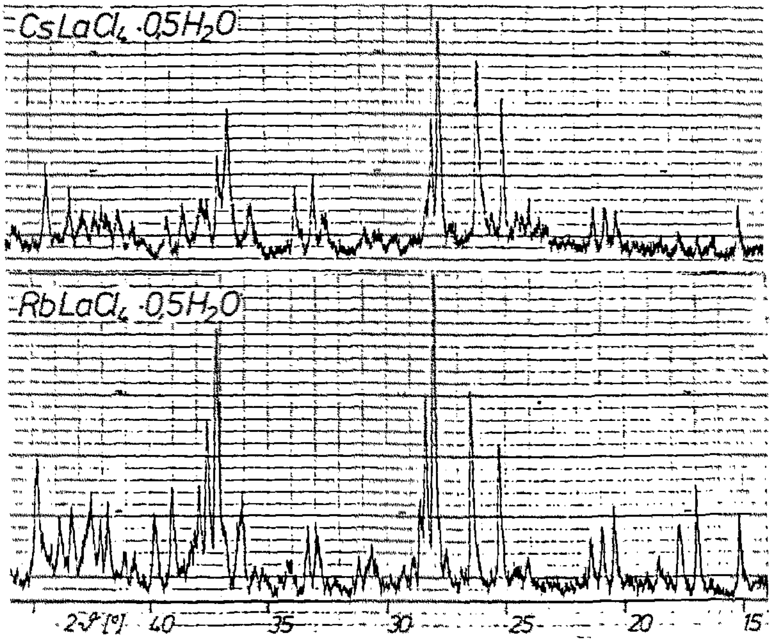

Fig. 2 X-ray powder diffractograms of semi-hydrates $ALaCl_4 \cdot 0.5H_2O$(A=Cs,Rb)

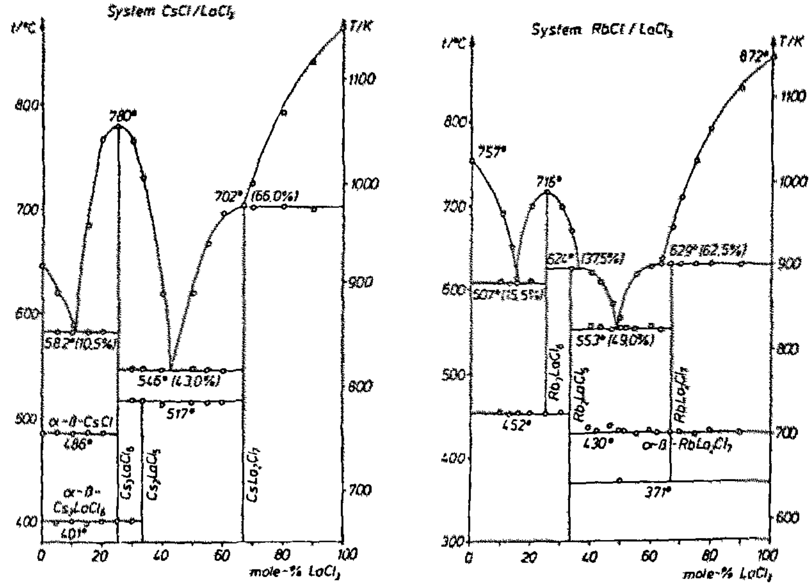

Fig. 3 Phase diagrams from DTA heating curves

DTA MEASUREMENTS

With the products of complete dehydration DTA-heating curves were measured. The results can be seen in fig.3. For the sample (Cs_2LaCl_5 + $CsLa_2Cl_7$) the first thermal effect was found at 517°C - the decomposition temperature of the 2:1-compound. - The mixture (Rb_2LaCl_5 + $LaCl_3$) revealed two effects in the solid state: at 371°C a strong endothermic peak indicates the formation of $RbLn_2Cl_7$; at 430°C a smaller peak followed, caused by the known non-reconstructive transition $\alpha \longrightarrow \beta$-$RbLa_2Cl_7$. In a second heating run the effect at 371°C did not appear any longer; during the foregone cooling process the compound has not decomposed because of kinetic hindrance. That the formation temperature of 371°C is nearly twenty degrees higher than the equilibrium temperature, found at 353°C by the EMF-measurement, is due to superheating, very common for solid state formation (and decomposition) reactions.

CONCLUSIONS

The investigations, described in this paper, were conducted to find a method for proving that the compound $RbLa_2Cl_7$ is not stable below 353° C as was found by EMF vs·T-measurements for the reaction 0.25 Rb_2LaCl_5 + 0.75 $LaCl_3$= $Rb_{0.5}LaCl_{3.5}$. Neither during the time of cooling in a DTA-measurement nor by annealing at ~320°C the decomposition did occur. Thus, the compound remains metastable also at ambient temperature. A prove for this metastability is given by the fact that the hydrate $RbLaCl_4 \cdot 0.5H_2O$ is not degradating into a mixture of Rb_2LaCl_5 and $RbLa_2Cl_7$ - such a 'disproportionation' occurs with the analogous compound $CsLaCl_4 \cdot 0.5H_2O$ - but Rb_2LaCl_5 and $LaCl_3$ is formed in such an intimate mixture, that in a DTA-heating run the formation temperature for $RbLa_2Cl_7$ from these two ingredients can be found.

It must be pointed out that by DSC the formation enthalpy could be determined too, but only one measurement is possible. After this the sample is irreversibly transformed to $RbLa_2Cl_7$.

Thus, we think to have done a little step for getting an answer to the question: What can be done to detect reactions at ambient or still lower temperature, where the mobility of the ions in the lattice has become so small, that nothing happens at all? It seems that then new preparative methods must be developed, which enable us to synthesize ternary chlorides, for instance, also at temperatures near T=O.

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